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Contents

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SOME AROMATICALLY SUBSTITUTED β-CHLOROPHENETOLES[1]

BY G. R. HARRIS AND ROSS STEWART[2]

Abstract

Six compounds derived from β-chlorophenetole have been synthesized from ethylene dichloride and the appropriate phenol. These are the *o*-methyl, *m*-methyl, *p*-methyl, *o*-methoxy, *p*-methoxy, and *o*-chloro derivatives of β-chlorophenetole.

In connection with polymerization studies on vinyl ethers it became necessary to prepare appreciable quantities of aromatically substituted β-chlorophenetoles as intermediates.

The method of synthesis adopted in this work is a modification of that of Wohl and Berthold (5). These workers prepared the parent compound, β-chlorophenetole (I), by heating equimolar quantities of phenol and ethylene dichloride to 110° C. with sodium hydroxide solution. It was found by the present authors, in agreement with a previous report on similar compounds (1), that under these conditions considerable amounts of ethylene glycol diphenyl ether were formed. The modified procedure entails the use of two moles of phenol and four moles of ethylene dichloride and was extended to six aromatically substituted phenols.

I R = H
II R = *o*-CH_3
III R = *m*-CH_3
IV R = *p*-CH_3
V R = *o*-CH_3O
VI R = *p*-CH_3O
VII R = *o*-Cl

The excess of ethylene dichloride serves a dual role: it reduces the formation of the corresponding ethylene glycol diphenyl ether to a negligible amount and it acts in the role of a solvent, allowing the product to be washed free of unreacted phenol with sodium hydroxide solution. This method is useful for preparing large quantities of these ethers in that it enables more moderate reaction temperatures to be employed than were required in the unmodified

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procedure (5). Although the yields are not high an exceedingly pure product is readily obtained. An increased ratio of the dichloride to the phenol (4 : 1) and longer refluxing periods had no effect on yields.

Experimental

The phenol (2 moles), ethylene dichloride (396 gm., 4 moles), potassium hydroxide (123 gm., 2.2 moles), and 300 ml. of water were heated under reflux for 26 hr. on the hot plate. The mixture was cooled, the layers separated (addition of water was sometimes required to effect a separation), and the oil layer was washed free of any unreacted phenol with hot 10% sodium hydroxide solution. The excess ethylene dichloride was removed by distillation and the residue was twice distilled, the second colorless distillate being collected over a one degree range. Those products that were solids were then crystallized from an ethanol–water mixture.

Results

The boiling points, yields, and analytical results for all of the products are listed in Table I.

TABLE I

No.	Name	B.p., °C.	Yield,* %	Formula	Analysis, % Cl†	
					Calc.	Found
II	*o*-Methyl-β-chlorophenetole‡	230–231	50	$C_9H_{11}OCl$	—	—
III	*m*-Methyl-β-chlorophenetole	235–236	50	$C_9H_{11}OCl$	20.79	20.69
IV	*p*-Methyl-β-chlorophenetole	236–237	46	$C_9H_{11}OCl$	20.79	20.73
V	*o*-Methoxy-β-chlorophenetole	254–255	55	$C_9H_{11}O_2Cl$	19.04	18.90
VI	*p*-Methoxy-β-chlorophenetole	286–287	55	$C_9H_{11}O_2Cl$	19.04	18.90
VII	*o*-Chloro-β-chlorophenetole§	251–252	55	$C_8H_8OCl_2$	37.10	37.06

* *All yields calculated on quantity of product obtained after second distillation over a one degree range.*

† *Method of Drogin and Rosanoff (4).*

‡ *Previously prepared by Clemo and Perkin (2), b.p. 227° to 229° C. (762 mm.).*

§ *Reported by Coleman and Stratton (3), b.p. 142° to 144° C. (21.5 mm.), no analysis given.*

The melting points and crystalline form of those products that were solids at room temperature are listed in Table II.

TABLE II

No.	M.p., °C.*	Crystalline form
IV	44 – 45	Colorless platelets
V	40 – 41	Colorless needles
VI	49 – 50	Colorless platelets

* *All melting points are corrected.*

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SYNTHESIS OF AMINO ACIDS FROM SUBSTITUTED CYANOACETIC ESTERS[1]

By Paul E. Gagnon and Benoit Nolin[2]

Abstract

α-Substituted cyanoacetic esters have been used to prepare hydrazides, azides, urethanes, and the 10 following α-amino acids: *dl*-α-aminocaprylic acid, *dl*-α-aminopelargonic acid, *dl*-α-aminocapric acid, *dl*-α-aminolauric acid, *dl*-α-(2-ethyl-*n*-butyl)-α-aminoacetic acid, *dl*-α-(2-ethyl-*n*-hexyl)-α-aminoacetic acid, *dl*-α-amino-γ-phenylbutyric acid, *dl*-α-amino-γ-benzylbutyric acid, *dl*-C-cyclohexylglycine, and *dl*-α-amino-β-1-naphthylpropionic acid. When a mixture of formic and hydrochloric acids and water was used, instead of hydrochloric acid, as hydrolyzing agent to transform the urethanes into amino acids, the period of heating was relatively short. The following compounds, as far as the authors are aware, have been prepared for the first time: ethyl α-cyanocaprylate, α-cyanocaprylamide, α-cyanocaprylic hydrazide, anisal α-cyanocaprylic hydrazide, benzal α-cyanocaprylic hydrazide, α-cyanocaprylic azide, α-carbethoxyaminocaprylonitrile, 5-(*n*-hexyl)-hydantoin, ethyl α-cyanopelargonate, α-cyanopelargonic hydrazide, anisal α-cyanopelargonic hydrazide, benzal α-cyanopelargonic hydrazide, isopropylidene α-cyanopelargonic hydrazide, α-cyanopelargonic azide, α-carbethoxyaminopelargonitrile, 5-(*n*-heptyl)-hydantoin, α-cyanocapric hydrazide, anisal α-cyanocapric hydrazide, benzal α-cyanocapric hydrazide, α-cyanocapric azide, α-carbethoxyaminocapronitrile, *dl*-α-phenylureidocapric acid, ethyl α-cyanolaurate, α-cyanolauric hydrazide, anisal α-cyanolauric hydrazide, α-cyanolauric azide, α-carbethoxyaminolauronitrile, *dl*-α-phenylureidolauric acid, ethyl-α-(2-ethyl-*n*-butyl)-α-cyanoacetate, α-(2-ethyl-*n*-butyl)-α-cyanoacetic hydrazide, anisal α-(2-ethyl-*n*-butyl)-α-cyanoacetic hydrazide, benzal α-(2-ethyl-*n*-butyl)-α-cyanoacetic hydrazide, α-(2-ethyl-*n*-butyl)-α-cyanoacetic azide, α-(2-ethyl-*n*-butyl)-α-carbethoxyaminoacetonitrile, *dl*-α-(2-ethyl-*n*-butyl)-α-aminoacetic acid, *dl*-α-(2-ethyl-*n*-butyl)-α-phenylureidoacetic acid, 5-(2-ethyl-*n*-butyl)-hydantoin, ethyl α-(2-ethyl-*n*-hexyl)-α-cyanoacetate, α-(2-ethyl-*n*-hexyl)-α-cyanoacetic hydrazide, anisal α-(2-ethyl-*n*-hexyl)-α-cyanoacetic hydrazide, α-(2-ethyl-*n*-hexyl)-α-cyanoacetic azide, α-(2-ethyl-*n*-hexyl)-α-carbethoxyaminoacetonitrile, *dl*-α-(2-ethyl-*n*-hexyl)-α-aminoacetic acid, 5-(2-ethyl-*n*-hexyl)-hydantoin, *dl*-α-(2-ethyl-*n*-hexyl)-α-phenylureidoacetic acid, ethyl α-cyano-γ-phenylbutyrate, α-cyano-γ-phenylbutyrhydrazide, anisal α-cyano-γ-phenylbutyrhydrazide, benzal α-cyano-γ-phenylbutyrhydrazide, α-cyano-γ-phenylbutyric azide, α-carbethoxyamino-γ-phenylbutyronitrile, 5-(β-phenylethyl)-hydantoin, *dl*-α-phenylureido-γ-phenylbutyric acid, ethyl α-cyano-γ-benzylbutyrate, α-cyano-γ-benzylbutyrhydrazide, anisal α-cyano-γ-benzylbutyrhydrazide, α-cyano-γ-benzylbutyric azide, α-carbethoxyamino-γ-benzylbutyronitrile, 5-(γ-phenylpropyl)-hydantoin, α-cyclohexyl-α-cyanoacetamide, α-cyclohexyl-α-cyanoacetic hydrazide, anisal α-cyclohexyl-α-cyanoacetic hydrazide, α-cyclohexyl-α-cyanoacetic azide, α-cyclohexyl-α-carbethoxyaminoacetonitrile, *dl*-α-cyclohexyl-α-phenylureidoacetic acid, ethyl α-cyano-β-1-naphthylpropionate, α-cyano-β-1-naphthylpropionhydrazide, anisal α-cyano-β-1-naphthylpropionhydrazide, α-cyano-β-1-naphthylpropionic azide, α-carbethoxyamino-β-1-naphthylpropionitrile, and *dl*-α-phenylureido-β-1-naphthylpropionic acid.

[1] *Manuscript received May 23, 1949.*

Contribution from the Department of Chemistry, Laval University, Quebec, Que. This paper constitutes a part of a thesis submitted to the Graduate School, Laval University, in partial fulfillment of the requirements for the degree of Doctor of Science.

[2] *Holder of a Canadian Industries Limited Research Scholarship and a Studentship under the National Research Council of Canada.*

Introduction

The decomposition of acid azides into isocyanates and nitrogen is known as the Curtius rearrangement. The reaction is a preparative method for isocyanates and compounds derived from them, such as urethanes, ureas, amides, and amines. When followed by hydrolysis, the Curtius rearrangement becomes a practical procedure for replacing a carboxyl group by an amino group. The whole process of converting an acid into its azide and an amine is commonly referred to as the Curtius reaction.

$$RCOOH \longrightarrow RCON_3 \longrightarrow RNCO \longrightarrow RNH_2$$

The synthesis of amino acids from substituted cyanoacetic esters by the Curtius reaction was first suggested by Darapsky and Hillers who synthesized glycine from cyanoacetic ester (2).

So far, 21 α-amino acids have been prepared by the Darapsky method (1, 4, 5, 6). The present paper deals with the synthesis of 10 other α-amino acids by the same method and is a contribution to the study of its general character.

The starting materials, the substituted cyanoacetic esters (I), were prepared by the condensation of organic halides with ethyl cyanoacetate in the presence of sodium ethylate. The yields varied from 45 to 78%.

I II III IV V

R = *n*-hexyl, $CH_3(CH_2)_5-$; *n*-heptyl, $CH_3(CH_2)_6-$; *n*-octyl, $CH_3(CH_2)_7-$; *n*-decyl, $CH_3(CH_2)_9-$; 2-ethyl-*n*-butyl, $CH_3CH_2CH(C_2H_5)CH_2-$; 2-ethyl-*n*-hexyl, $CH_3(CH_2)_3CH(C_2H_5)CH_2-$; β-phenylethyl, $C_6H_5(CH_2)_2-$; γ-phenylpropyl, $C_6H_5(CH_2)_3-$; cyclohexyl, $C_6H_{11}-$; 1-methylnaphthyl, $C_{10}H_7CH_2-$.

The formation of hydrazides (II) from the starting materials took place at room temperature merely by mixing the esters (I) with hydrazine hydrate. All the hydrazides were identified by condensing them with suitable reagents.

The conversion of the hydrazides into the corresponding azides (III) took place smoothly by treatment with nitrous acid, the azides being extracted with ether. On boiling the alcoholic solutions of the azides under reflux, the ethyl urethanes were formed.

The hydrolysis of the urethanes with hydrochloric acid required long periods of heating to get the highest possible yields in amino acids (V). In two cases, a mixture of equal volumes of concentrated hydrochloric acid, formic acid (85%), and water was used to obtain better yields.

TABLE I

ETHYL α-SUBSTITUTED CYANOACETATES, $RCH(CN)COOC_2H_5$

R	Starting material	Yield, %	B.p., °C.	Formula	Nitrogen, %		$n_D^{°C.}$
					Calc.	Found	
n-Hexyl	$CH_3(CH_2)_5Br$	70	149–150 (19 mm.)	$C_{11}H_{19}O_2N$	7.10	7.17	1.4319^{23}
n-Heptyl	$CH_3(CH_2)_6Br$	70	144–147 (12 mm.)	$C_{12}H_{21}O_2N$	6.57	6.70	1.4345^{22}
n-Octyl*	$CH_3(CH_2)_7Br$	75	159–162 (15 mm.)	$C_{13}H_{23}O_2N$	6.22	6.37	1.4381^{22}
n-Decyl	$CH_3(CH_2)_9Br$	65	148–150 (5 mm.)	$C_{15}H_{27}O_2N$	5.53	5.76	1.4429^{26}
2-Ethyl-*n*-butyl	$CH_3CH_2CH(C_2H_5)CH_2Br$	50	138–142 (19 mm.)	$C_{11}H_{19}O_2N$	7.10	7.26	1.4333^{24}
2-Ethyl-*n*-hexyl	$CH_3(CH_2)_3CH(C_2H_5)CH_2Br$	50	118–122 (4 mm.)	$C_{13}H_{23}O_2N$	6.22	6.50	1.4390^{24}
β-Phenylethyl	$C_6H_5(CH_2)_2Br$	78	163–165 (7 mm.)	$C_{13}H_{15}O_2N$	6.45	6.55	1.5030^{16}
γ-Phenylpropyl	$C_6H_5(CH_2)_3Br$	68	175–177 (10 mm.)	$C_{14}H_{17}O_2N$	6.05	6.17	1.4975^{26}
Cyclohexyl**	$C_6H_{11}Br$	23	125–127 (8 mm.)	—	—	—	1.4580^{25}
1-Methylnaphthyl	$C_{10}H_7CH_2Cl$	45	146–148 (0.005 mm.)	—	—	—	1.5690^{24}

* *Ref. (7).* ** *Ref. (3).*

The following α-amino acids were prepared in yields varying from 35 to 53%: *dl*-α-aminocaprylic acid, *dl*-α-aminopelargonic acid, *dl*-α-aminolauric acid, *dl*-α-(2-ethyl-*n*-butyl)-α-aminoacetic acid, *dl*-α-(2-ethyl-*n*-hexyl)-α-aminoacetic acid, *dl*-α-amino-γ-phenylbutyric acid, *dl*-α-amino-γ-benzylbutyric acid, *dl*-C-cyclohexylglycine and *dl*-α-amino-β-1-naphthylpropionic acid.

This result and those previously reported in the literature clearly indicate that the Darapsky method for the synthesis of α-amino acids is of wide application.

Experimental*

Substituted Cyanoacetic Esters (I)

To a solution of sodium ethoxide (400 ml. of absolute ethyl alcohol per mole of sodium) were added two equivalents of ethyl cyanoacetate and one equivalent of organic halide while cooling. The reaction mixture was boiled under reflux on a water bath until it was neutral to wet litmus paper. The alcohol was removed by distillation and the residue poured into cold water. The oily layer formed was decanted and the aqueous layer, previously acidified, was extracted several times with ether. The oily layer and the ethereal solutions were dried over anhydrous sodium sulphate, the ether evaporated, and the residue distilled under reduced pressure.

The properties and yields of the esters are summarized in Table I.

Substituted Cyanoacethydrazides (II)

The substituted cyanoacetates were stirred at room temperature with one equivalent of hydrazine hydrate (100%); heat was evolved. The reaction mixtures were allowed to stand in an evacuated desiccator over phosphorus pentoxide to eliminate the alcohol formed. Most of the hydrazides solidified and were crystallized from ethanol. Their properties are given in Table II.

TABLE II

α-SUBSTITUTED CYANOACETHYDRAZIDES, $RCH(CN)CONHNH_2$

R	M.p., °C.	Formula	Nitrogen, %	
			Calc.	Found
n-Hexyl	69–70	$C_9H_{17}ON_3$	22.93	23.03
n-Heptyl	89–90	$C_{10}H_{19}ON_3$	21.30	21.57
n-Octyl	80–81	$C_{11}H_{21}ON_3$	19.88	19.99
n-Decyl	89–90	$C_{13}H_{25}ON_3$	17.56	17.32
β-Phenylethyl	90–91	$C_{11}H_{13}ON_3$	20.67	20.62
γ-Phenylpropyl	89–90	$C_{12}H_{15}ON_3$	19.34	19.25

* *All melting points are uncorrected.*

Derivatives of Substituted Cyanoacethydrazides

All the hydrazides were identified by their condensation products with anisaldehyde, benzaldehyde, or acetone. The properties of the derivatives are listed in Table III.

TABLE III

ANISAL, BENZAL, AND ISOPROPYLIDENE DERIVATIVES

Compound	M.p., °C.	Formula	Nitrogen, %	
			Calc.	Found
$RCH(CN)CONHN{=}CHC_6H_4OCH_3$				
R = *n*-Hexyl	109–110	$C_{17}H_{23}O_2N_3$	13.94	13.69
n-Heptyl	106–108	$C_{18}H_{25}O_2N_3$	13.32	13.51
n-Octyl	105–106	$C_{19}H_{27}O_2N_3$	12.75	12.82
n-Decyl	109–110	$C_{21}H_{31}O_2N_3$	11.76	11.92
2-Ethyl-*n*-butyl	130–131	$C_{17}H_{23}O_2N_3$	13.94	14.00
2-Ethyl-*n*-hexyl	89– 90	$C_{19}H_{27}O_2N_3$	12.75	12.77
β-Phenylethyl	145–147	$C_{19}H_{19}O_2N_3$	13.07	13.01
γ-Phenylpropyl	129–130	$C_{20}H_{21}O_2N_3$	12.53	12.49
Cyclohexyl	178–180	$C_{17}H_{21}O_2N_3$	14.03	14.19
1-Methylnaphthyl	174–175	$C_{22}H_{19}O_2N_3$	11.72	11.42
$RCH(CN)CONHN{=}CHC_6H_5$				
R = *n*-Hexyl	72– 73	$C_{16}H_{21}ON_3$	15.52	15.60
n-Heptyl	81– 82	$C_{17}H_{23}ON_3$	14.73	14.67
n-Octyl	70– 71	—	—	—
2-Ethyl-*n*-butyl	87– 88	—	—	—
β-Phenylethyl	129–130	$C_{18}H_{17}ON_3$	14.94	14.77
$RCH(CN)CONHN{=}C(CH_3)_2$				
R = *n*-Heptyl	80– 81	$C_{13}H_{23}ON_3$	17.70	17.72

Amino Acids (V)

The substituted cyanoacethydrazides were transformed into the azides as originally outlined by Darapsky (1). The aqueous suspensions of the hydrazides were treated in the cold with nitrous acid and the azides extracted with ether. To the ethereal solutions, ethanol was added. The ether was evaporated and the resulting alcoholic solutions refluxed for about one hour. After the removal of the alcohol, the crude urethanes were obtained as pale or dark brown liquids.

The urethanes were hydrolyzed with two different agents: hydrochloric acid (20%) or a mixture of equal volumes of concentrated hydrochloric acid, formic acid (85%), and water. The amino acids were isolated by neutralizing, with dilute ammonia, solutions in water of their purified hydrochlorides.

The properties and yields of the amino acids together with the properties of their derivatives are given in Table IV.

TABLE IV

AMINO ACIDS AND DERIVATIVES

Compound	Hydrolyzing agent	Time, hr.	Yield, %	Derivative	M.p., ° C.	Formula	Nitrogen, %	
							Calc.	Found
dl-α-aminocaprylic acid	20% HCl	84	35	hydantoin	147–148	$C_9H_{16}O_2N_2$	15.20	15.28
dl-α-aminopelargonic acid	20% HCl	85	47	hydantoin	142	$C_{10}H_{18}O_2N_2$	14.13	14.48
dl-α-aminocapric acid	20% HCl	88	53	phenylureido	128–129	$C_{17}H_{24}O_3N_2$	9.14	9.33
dl-α-aminolauric acid	mixed acids	69	41	phenylureido	127–128	$C_{19}H_{28}O_3N_2$	8.38	8.51
dl-α-(2-ethyl-*n*-butyl)-α-aminoacetic acid	20% HCl	108	34	phenylureido*	131–132	$C_{18}H_{26}O_3N_2$	10.06	10.24
dl-α-(2-ethyl-*n*-hexyl)-α-aminoacetic acid	20% HCl	108	40	hydantoin**	123–124	$C_{11}H_{20}O_2N_2$	13.19	13.34
dl-α-amino-γ-phenylbutyric acid	mixed acids	24	34	hydantoin†	167–168	$C_{11}H_{12}O_2N_2$	13.71	13.97
dl-α-amino-γ-benzylbutyric acid	20% HCl	84	38	hydantoin	158–159	$C_{12}H_{14}O_2N_2$	12.83	12.98
dl-C-cyclohexylglycine	20% HCl	48	45	phenylureido	190	$C_{15}H_{20}O_3N_2$	10.14	10.31
dl-α-amino-β-1-naphthylpropionic acid	20% HCl	68	20	phenylureido	145–146	$C_{20}H_{18}O_3N_2$	8.38	8.64

* *Hydantoin, m.p. 189° C.*
** *Phenylureido, m.p. 129–130° C.*
† *Phenylureido, m.p. 173° C.*

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VARIATIONS DES TENEURS EN GLYCOGÈNE ET EN TRÉHALOSE PENDANT LE SÉCHAGE DE LA LEVURE[1]

PAR ROGER PAYEN

Sommaire

La transformation des glucides de la levure pendant sa dessiccation a été étudiée. Une méthode de dosage du glycogène est proposée, dans laquelle l'alcool méthylique remplace l'alcool éthylique pour la précipitation. Pendant le séchage de la levure, la teneur en glucides totaux de la cellule change peu, alors que le glycogène disparaît presque complètement. Il semble que du tréhalose, formé pendant la dessiccation de la levure, prend la place du glycogène.

Introduction

Le but du présent travail était d'étudier les variations dans la teneur en glucides se produisant pendant le séchage de la levure préparée spécialement pour l'obtention des levures sèches vivantes de boulangerie.

Les principaux constituants glucidiques de la levure sont le glycogène (1), la gomme de levure ou mannane (7), le tréhalose (10), et un polyose, le glucane-1,3 (3, 11). Des méthodes de dosage pour le glycogène (3, 4, 5, 9), la mannane (2, 4, 9) et le tréhalose (8, 10), ont été proposées, mais elles laissent toutes plus ou moins à désirer.

Les procédés actuels d'extraction des glucides de la levure avec de l'hydroxyde de potassium à 60–85%, suivie d'une précipitation de l'extrait par l'alcool éthylique, donnent un mélange contenant au moins la gomme de levure et le glycogène. Deux méthodes ont été suggérées pour estimer séparément ces deux constituants. La première, due à Mayer (5), sépare le glycogène d'avec la mannane en saturant la solution contenant les deux glucides par le sulfate d'ammonium, ce qui précipite le glycogène. La deuxième méthode précipite la mannane sous forme de complexe cuivrique, au moyen de la liqueur de Fehling. Cette dernière méthode a été utilisée par Ling, Nangi et Paton (4), Hashitani (2), puis perfectionnée par Stockhausen et Silbereisen en 1935 (9). Le glycogène et la mannane ainsi séparés sont ensuite hydrolysés par un acide et les sucres réducteurs dosés.

Les méthodes de dosage du tréhalose consistent soit à extraire la levure par l'alcool à 90%, puis à laisser cristalliser l'extrait (10), soit à extraire la levure avec une solution normale d'acide sulfurique (8) ou avec de l'alcool à 90% et à doser les sucres réducteurs présents après hydrolyse acide de l'extrait.

Résultats expérimentaux

Dosage du glycogène

Au cours de nos recherches, nous avons eu l'occasion de comparer les résultats obtenus en dosant le glycogène de la levure par la méthode de

[1] *Manuscrit reçu le 5 avril 1949.*

Contribution du l'Institut de Chimie de la Faculté des Sciences, Université de Montréal, Montréal, Qué.

Stockhausen (9), avec ceux que donne la méthode colorimétrique à l'iode (6). La différence très grande obtenue entre les valeurs trouvées par les deux méthodes dépasse de beaucoup les erreurs possibles d'analyse.

TABLEAU I

TENEURS EN GLYCOGÈNE OBTENUES PAR DEUX MÉTHODES DIFFÉRENTES

Levure N°	Méthode Stockhausen, %	Méthode colorimétrique, %
19 pressée	16.36	7.0
30 séchée	6.51	0.4
31 "	9.77	0.8
33 "	7.78	1.0
41 "	14.16	2.0

La méthode Stockhausen consiste à précipiter le glycogène de sa solution alcaline en amenant celle-ci à une concentration d'environ 75% en alcool éthylique. Nous avons constaté que la quantité de glycogène obtenue par cette méthode diminue beaucoup, si l'on reprécipite le glycogène une deuxième fois.

TABLEAU II

VARIATION DE LA TENEUR EN GLYCOGÈNE AVEC LE NOMBRE DE PRÉCIPITATIONS

Levure N°	Glycogène après une précipitation, %	Glycogène après deux précipitations, %
41	14.16	6.98

L'alcool méthylique précipite également le glycogène quantitativement de ses solutions alcalines, quand on en utilise deux volumes pour un de solution. Ainsi, des dosages de glycogène sur des foies d'animaux ont donné les résultats suivants:

TABLEAU III

COMPARAISON ENTRE L'ALCOOL MÉTHYLIQUE ET L'ALCOOL ÉTHYLIQUE COMME AGENT DE PRÉCIPITATION DU GLYCOGÈNE

Source du glycogène	Glycogène précipité par l'alcool éthylique (1 précipitation), %	Glycogène précipité par l'alcool méthylique (1 précipitation), %
Foie de rat (Traité immédiatement après la mort de l'animal)	2.37	2.40
Foie de veau (Conservé à la glacière)	0.48	0.45

Nous avons également traité un extrait alcalin de levure au moyen de deux volumes d'alcool méthylique. Le précipité obtenu a été séparé par filtration, et le filtrat distillé en partie afin de le débarrasser de l'alcool méthylique. Le résidu, additionné d'alcool éthylique, donne un précipité qui ne contient pas de glycogène ni de mannane, comme le montrent l'absence de coloration par l'iode et l'absence de précipité quand on sature la solution avec du sulfate d'ammonium ou qu'on lui ajoute de la liqueur de Fehling.

Nous avons donc modifié la méthode proposée par Stockhausen et nous décrivons notre méthode à la fin de ce travail.

L'analyse de différentes levures pressées ou séchées, obtenue en utilisant l'alcool méthylique, est donnée dans le tableau IV, à côté des résultats donnés par la méthode utilisant l'alcool éthylique.

TABLEAU IV

TENEURS EN GLYCOGÈNE OBTENUES EN CHANGEANT L'AGENT DE PRÉCIPITATION

Levure N°	Glycogène précipité par l'alcool éthylique, %	Glycogène précipité par l'alcool méthylique, %
19 pressée	16.36	6.18
20 "	13.95	8.14
30 séchée	6.51	0.93
31 "	9.77	2.25
33 "	7.78	2.49
41 "	14.16	3.23

La différence entre les résultats obtenus par les deux méthodes représente un glucide différent du glycogène et de la mannane. Comme les conditions de précipitation du glycogène par trois volumes d'alcool éthylique dans la méthode Stockhausen pourraient favoriser la cristallisation du tréhalose, qui dans certaines levures représente jusqu'à 18% de la matière sèche, ce qui expliquerait les chiffres trop élevés obtenus pour le glycogène, nous avons fait des expériences avec des mélanges de glycogène pur et de tréhalose. Ces expériences démontrent que le tréhalose ne se sépare pas avec le glycogène, pendant la précipitation de ce dernier par la méthode de Stockhausen.

1° expérience. 0.075 g. de glycogène + 0.1125 g. de tréhalose; trouvé 0.077 g. de glycogène.

2° expérience. 0.060 g. de glycogène + 0.1260 g. de tréhalose; trouvé 0.054 g. de glycogène.

Les quantités de tréhalose ajoutées dans ces essais correspondaient à des teneurs respectives de 15 et 17% en tréhalose dans la levure.

La préparation de la levure sèche vivante pour la boulangerie, à partir de levures cultivées spécialement dans ce but, est accompagnée d'une diminution très marquée de la teneur en glycogène, telle que mesurée par notre méthode de dosage.

TABLEAU V

VARIATION DE LA TENEUR EN GLYCOGÈNE PENDANT LA DESSICCATION

Levure N°	Glycogène avant séchage, %	Glycogène après séchage, %
19	6.18	1.21
20	8.14	2.76
21	4.86	1.55

En général, du reste, les levures séchées ont toujours une teneur en glycogène très faible (voir tableau I).

D'autre part, la teneur en glucides totaux de la levure ne diminue pratiquement pas pendant le séchage. Il en est de même pour la teneur en glucides autofermentescibles de la cellule.

TABLEAU VI

VARIATION DE LA TENEUR EN GLUCIDES DE LA LEVURE PENDANT LA DESSICCATION

Levure N°	Avant séchage, %	Après séchage, %
*Glucides totaux**		
20	36.74	36.20
21	36.32	35.43
30	29.44	29.90
43	24.13	24.60
*Glucides autofermentescibles**		
21	18.49	17.81

**Calculés en glucose.*

La perte en glycogène observée après dessiccation de la levure doit donc être en partie compensée par la formation d'un autre glucide dans la cellule, et il semble en effet que du tréhalose prend naissance en quantité à peu près équivalente au glycogène disparu.

Dosage du tréhalose

Pour doser le tréhalose, nous avons extrait la levure pressée ou séchée par l'alcool à 90% au reflux. L'extrait alcoolique était ensuite mis à cristalliser. La cristallisation quantitative du tréhalose est incertaine, mais cette méthode donne au moins la certitude que les valeurs obtenues se rapportent au glucide étudié. Il est remarquable que les levures sèches vivantes contiennent toutes plus de tréhalose que les levures pressées.

TABLEAU VII

TENEUR EN TRÉHALOSE DE LA LEVURE DE BOULANGERIE

Levure N°	Tréhalose, %	Levure N°	Tréhalose, %
22 pressée	3.6	31 séchée	8.6
27 "	3.5	33 "	7.8
20 séchée	6.8	39 "	6.2
30 "	5.8	41 "	18.0

Des levures,* étudiées avant et après séchage, ont donné les résultats suivants.

TABLEAU VIII

VARIATION DES TENEURS EN GLUCIDES DE LA LEVURE PENDANT LA DESSICCATION

Levure N°	Glucides étudiés	Avant séchage, %	Après séchage, %
20	Glucides totaux	36.74	36.20
	Glycogène	8.14	2.76
	Tréhalose	2.50	6.50
21	Glucides totaux	36.32	35.43
	Glucides autofermentescibles	18.49	17.81
	Glycogène	4.86	1.55
	Tréhalose	3.50	6.70

Conclusions

La levure de boulangerie préparée spécialement pour la fabrication des levures sèches vivantes perd, pendant la dessiccation, la majeure partie de son glycogène. Toutefois, du tréhalose prend naissance pendant le séchage de la levure si bien que la teneur en glucides totaux ne diminue presque pas.

Méthodes d'Analyse

1. Dosage des glucides donnant un sucre réducteur après hydrolyse acide

Placer 1.5 g. de levure sèche et 5 ml. d'eau, ou bien 5 g. de levure pressée, dans une fiole conique de 125 ml. Ajouter 10 ml. d'acide chlorhydrique concentré et 70 ml. d'eau. Tenir au bain-marie bouillant, sous reflux, pendant trois heures. Refroidir. Neutraliser par la soude caustique, en présence de phénolphtaléine, en refroidissant, et en évitant tout excès d'alcali, puis décolorer par quelques gouttes d'acide acétique.

Déféquer la solution en ajoutant 10 ml. d'une solution saturée d'acétate neutre de plomb, diluer à 100 ml. exactement puis laisser déposer quelques heures.

* *Levure cultivée dans les laboratoires de l'Université de Montréal à partir de la levure pressée de boulangerie commerciale F. A. Lallemand.*

Filtrer sur papier Whatman N° 40. Prélever 50 ml. du filtrat, dans un flacon jaugé de 100 ml. Ajouter 10 ml. d'une solution saturée d'oxalate de potassium, compléter à 100 ml., puis filtrer.

Prélever 50 ml. du filtrat pour le dosage des sucres réducteurs d'après la méthode de Munson et de Walker.

2. Dosage des glucides autofermentescibles

Placer dans une fiole conique de 125 ml., 5 g. de levure pressée ou 1.5 g. de levure séchée avec 15 ml. d'eau distillée et 2 à 3 ml. d'éther éthylique. La levure est laissée en contact 48 h. en renouvelant l'éther si nécessaire, puis elle est ensuite hydrolysée et les sucres réducteurs non fermentés dosés d'après la méthode I.

La différence entre les sucres réducteurs trouvés par la méthode I et ceux après autofermentation représente les glucides autofermentescibles.

3. Dosage du glycogène après hydrolyse acide

Dans une fiole conique de 250 ml., on place 6 g. de levure sèche et 14 ml. d'eau, ou 20 g. de levure pressée. On ajoute 60 ml. d'une solution d'hydroxyde de potassium (65 g. d'hydroxyde de potassium avec 35 ml. d'eau). On met à refluer, très doucement au debut, pendant trois heures.

Le mélange est refroidi, dilué exactement à 100 ml., puis additionné d'un peu de terre à diatomées. On filtre sur papier Reeve Angel N° 202, en couvrant l'entonnoir et le flacon receveur afin de diminuer l'évaporation.

On prélève une portion de 50 ml., dans laquelle on précipite la gomme et le glycogène par 100 ml. d'alcool méthylique et un cristal d'acétate de sodium. Il précipite immédiatement des grumeaux blancs. On laisse reposer une nuit, puis le précipité est décanté sur un papier filtre Whatman N° 40. On lave trois fois le précipité avec de l'alcool méthylique à 75% contenant un peu d'acétate de sodium.

Le précipité est ensuite dissous dans une solution d'hydroxyde de potassium à 2% chaude, et le papier filtre lavé également avec la solution alcaline à 2%. On dilue à 100 ml. dans un flacon jaugé. (Solution A).

(*a*) *Dosage de la gomme et du glycogène*

Prélever exactement 50 ml. de la solution A, ajouter 9 ml. d'acide chlorhydrique concentré et 21 ml. d'eau. Tenir sous reflux, au bain-marie pendant trois heures. Refroidir et continuer comme pour le dosage des glucides tel que décrit dans la méthode I.

(*b*) *Dosage de la gomme*

Prélever 40 ml. de la solution A, puis ajouter 80 ml. de liqueur de Fehling froide, tel que décrit par Stockhausen et Silbereisen (9). Filtrer sur papier

Whatman N° 40, après avoir laissé reposer pendant une nuit, et laver avec une solution d'hydroxyde de potassium à 2%.

Dissoudre le résidu avec un mélange de 9 ml. d'acide chlorhydrique concentré et 71 ml. d'eau. Hydrolyser au bain-marie sous reflux pendant trois heures. Procéder ensuite au dosage des sucres réducteurs tel que décrit pour la méthode I.

L'équivalent-glucose du glycogène est calculé par différence; on obtient la valeur exacte en glycogène en multipliant par le facteur 0.927 (9).

4. *Dosage colorimétrique du glycogène*

On utilise 20 ml. de l'extrait alcalin tel qu'obtenu par digestion de la levure avec la solution concentrée d'hydroxyde de potassium (voir méthode I).

Le glycogène, avec d'autres glucides, est précipité à deux reprises, par trois volumes d'alcool éthylique et un peu d'acétate de sodium.

On dissout le précipité dans 20 ml. d'eau distillée, on acidifie avec un peu d'acide chlorhydrique, et on ajoute 10 gouttes d'une solution d'iode décinormale. La coloration brune produite est comparée avec celle donnée par un poids connu de glycogène pur.

5. *Dosage du tréhalose*

On place 25 g. de levure sèche dans un extracteur Soxhlet modifié, surmonté d'un premier réfrigérant sec servant de réchauffeur et d'un deuxième réfrigérant dans lequel circule l'eau de condensation. On fait refluer avec 100 ml. d'alcool à 80% pendant 15 h. environ.

Le contenu du ballon d'extraction est refroidi afin de précipiter des substances gommeuses jaunâtres (A), puis la solution alcoolique décantée, ajustée à une concentration d'alcool de 90% environ est mise à la glacière pendant une semaine.

Le résidu gommeux (A) précipité est extrait de nouveau sous reflux pendant quelques heures par de l'alcool à 90% afin d'enlever le trêhalose entraîné, puis la solution refroidie et décantée, est également placée à la glacière pendant une semaine. Après ce temps les cristaux sont recueillis, lavés à l'alcool à 90% froid, puis par de l'éther. Ils sont ensuite séchés rapidement à l'air.

Pour les levures préssées, l'extraction du tréhalose est plus difficile. On prend 100 g. de levure pressée et on ajoute assez d'alcool à 95% pour avoir une solution d'alcool à 90%. On fait refluer plusieurs heures et on filtre. Le résidu est repris de nouveau par l'alcool à 90%. Les extraits combinés sont distillés sur bain-marie, puis le résidu gommeux est extrait à deux reprises sous reflux par l'alcool éthylique à 90% bouillant. On met à cristalliser ensuite comme pour la levure séchée.

Dans les deux cas, il faut ajouter un facteur de correction correspondant à la solubilité du tréhalose dans l'alcool à la température de cristallisation.

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THE EXTRACTION AND PURIFICATION OF XENON AND KRYPTON ISOTOPES FROM NEUTRON IRRADIATED URANIUM[1]

By W. J. Arrol,[2] K. F. Chackett,[3] and S. Epstein[4]

Abstract

Both long-lived and stable isotopes of krypton and xenon are formed as the result of the slow neutron fission of uranium 235. A method is described for the extraction of these gases from massive neutron irradiated uranium metal, for separating them from contaminating gases and from each other and measuring them in a McLeod gauge, the amounts of uranium being of the order of 50 gm. and the rare gases of the order of 10^{-3} cc. at N.T.P. An accurate value of the ratio of fission xenon to fission krypton is given. Further experiments concern Geiger–Müller counter measurements on the long-lived krypton isotope.

Introduction

As long-lived or stable xenon isotopes were known to occur in, or at the end of, several fission chains, a program was initiated to extract, purify, and examine macro quantities of xenon gas from pile irradiated uranium. The mass spectrometric examination of the final samples has already been reported on by Thode and Graham (3).

It was expected that samples of the order of 10^{-3} cc. at N.T.P. would be obtained from 30 to 50 gm. of the uranium available. Argon, probably occluded during the preparation of the metal, was found to be present in the extracted gases in considerable quantity. Preliminary tests by Thode and Graham indicated that argon, krypton, and xenon were all present, and also a mass 85—presumably a long-lived krypton isomeric with 4.0 hr. krypton 85.

A program was then initiated to extract all the rare gases, separate the argon, xenon, and krypton fractions, estimate them individually to $\pm$ 0.5%, examine them for long-lived radioactive isotopes, and submit them to mass spectrometric examination (3).

Experimental

Specimens of pure uranium metal were prepared in the form of disks about 1.1 in. in diameter, weighing between 20 and 50 gm. Twenty disks were made up into a cylindrical composite "slug", which was sealed into an aluminum sheath and pile irradiated. In order to avoid unnecessary handling of the disks after irradiation (because even after six months they were still appreciably radioactive) the disks were all weighed before irradiation and their weights stamped on them with punches. About 15 disks were kept unirradiated for blank experiments.

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Massive uranium metal was found to dissolve in a controllable manner in saturated potassium cuprichloride solution with the evolution of some hydrogen which was sufficient to act as a convenient carrier for sweeping the rare gases through the drying train. The gas extraction apparatus is shown in Fig. 1.

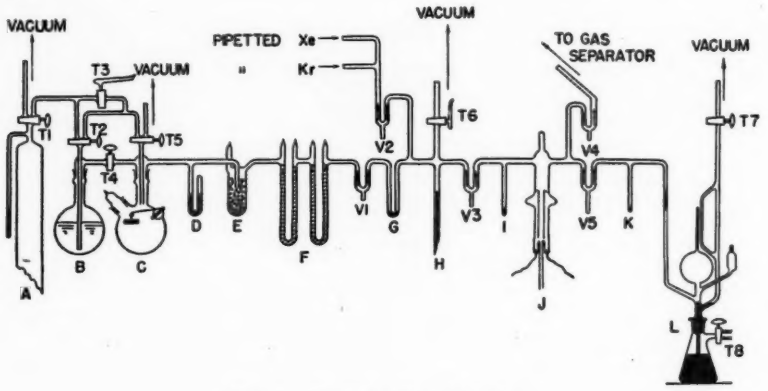

FIG. 1. *Gas extraction apparatus.*

Vessels *B* and *C* were of 1 liter capacity, and about 600 cc. of a saturated potassium cuprichloride solution in *B* was swept clean of dissolved air with pure hydrogen from reservoir *A* passing through T_1, T_2, T_4, and T_5 to vacuum. The solution was then transferred to the evacuated reaction vessel *C* through T_2 and T_5. A platinum wire basket was suspended from a rotating arm in *C* whose movement could be controlled from outside the vacuum system through a greased cone and socket joint. This basket containing the uranium metal specimen could thus be lowered into the solution and, if the reaction became too vigorous or if the manometers *D* and *H* indicated too high pressure in the system, hoisted out again.

The gas mixture from the uranium dissolution consisted of a relatively large amount of hydrogen and water vapor, traces of hydrocarbons from uranium carbides, and the small amounts of rare gases. This mixture passed through a rough drying trap, *E*, containing pellets of solid potassium hydroxide, through two U-tubes, *F*, of anhydrous magnesium perchlorate and finally through a charcoal trap, *G*, cooled in liquid air, where all the gases were adsorbed except hydrogen, which passed through and was pumped away through T_6. From this point onward where the gases had been separated from their carrier, they were manipulated by standard high vacuum technique in part of the apparatus in which mercury ventils (V_1–V_5) replaced stopcocks in order to avoid possible loss of xenon and krypton in grease.

By warming *G* and cooling the small charcoal tube, *I*, the mixture of hydrocarbons and rare gases (sometimes with some hydrogen) was transferred into a section of the apparatus containing a calcium furnace (Fig. 2) after the

original of Soddy (2), except that it was in a sealed Pyrex envelope completely free from grease. *A* was the calcium metal in a stainless steel thimble, *B*. A 90% Pt – 10% Rh flat filament, *D*, was wound into a spiral cut in a fused silica support, *C*. Leads to the furnace entered the envelope, *F*, through tungsten seals and were fitted to nickel tubes, *E*. The connections were made with tweezers through side tubes in the envelope, which were afterwards

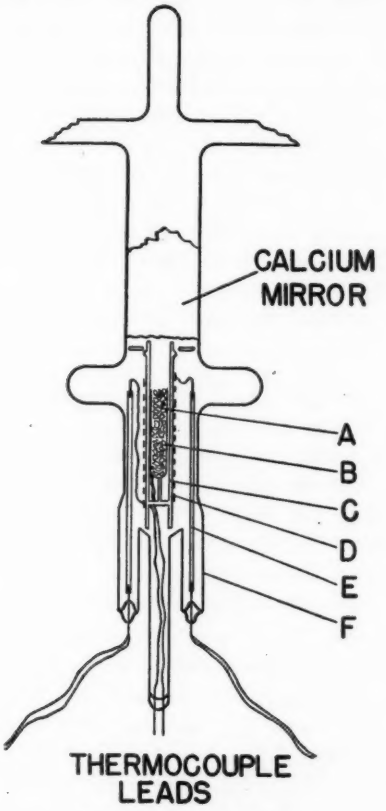

FIG. 2. *Calcium furnace.*

sealed off. The sealed-off tube on top of the furnace could be opened and a fresh charge of calcium metal introduced without remaking the furnace. The gas mixture was subjected to calcium vapor at temperatures between 450° and 500° C. for about 20 min. Calcium forms solid products with all gases except the rare gases, and after a time, which was usually about 20 to 30 min., the rare gases were shown spectroscopically to be free from hydrogen, hydrocarbon, or any other impurity. The gases were transferred to the McLeod gauge by adsorbing them in charcoal tube *K*.

Gas measurements were carried out in a McLeod gauge (Fig. 1, *L*) of special design. The capillaries were about 2.5 mm. I.D. and the closed capillary was calibrated with mercury. A small side bulb connected below the main bulb took off a sample of the contents of the McLeod gauge which could be contained in a capillary tube at the top, excited with a Tesla coil, and the spectrum examined. Absolute calibration of the McLeod gauge was carried out using measured quantities of krypton and xenon pipetted into the apparatus through V_2 at known temperature and pressure. Instead of tapping capillaries of the gauge by hand, these were vibrated by an electrically driven reed and the mercury levels were then measured using a travelling microscope. With these refinements an accuracy of $\pm$ 0.5% was obtainable in the measurements of amounts of gas of not less than 0.5 cu. mm. at N.T.P.

Before the irradiated uranium was used, the apparatus was tested rigorously on samples of pure rare gases of the order of the amounts expected from fission. No losses were observed when samples of krypton and xenon were treated repeatedly with calcium vapor. This showed that the gases were not trapped in the mirror of calcium condensing out on the walls of the furnace. In other experiments, known amounts of argon, krypton, and xenon were condensed separately into a small charcoal tube sealed temporarily to the vessel in which the uranium was to be dissolved. The proposed extraction procedure was then followed, using a stream of pure hydrogen admitted through T_1, T_3, and T_5 in place of the hydrogen which would have been evolved during solution of the metal. In different experiments, widely different flow speeds of hydrogen were used, and in each case krypton and xenon were recovered quantitatively. Even in the case of the less condensable argon, the final amount recovered was within 1% of the original. Blank experiments on the hydrogen used showed no trace of rare gas, but, as has already been pointed out, blank experiments on unirradiated uranium showed the presence of argon.

Because of the occurrence of argon and krypton in the gas mixture extracted from irradiated uranium, it was desirable to have methods for their quantitative analysis. Estimates of the relative amounts of the gases could be made from mass spectroscopic data, but, as Thode and Graham point out (3), difficulties are involved owing to fractionation of small quantities of the gases in the fine capillary leak leading into the ion source of the instrument and also to differences in ionization potentials. It was therefore decided to carry out the direct separation of argon, krypton, and xenon and measurement of the fractions in the McLeod gauge.

For this purpose, a new section of apparatus was built communicating through a ventil to the calcium furnace. It consisted of a fractional adsorption system of nine units, in many respects similar to one described by Dr. E. Glückauf* for the separation of helium and neon. The fact that argon, krypton, and xenon can all be adsorbed completely on charcoal at liquid

** The work of Glückauf was carried out in London in 1938, and, although not published in detail until 1946, was known to the authors in 1945.*

nitrogen temperature made slight simplifications possible. U-tubes containing about 0.08 gm. of charcoal each and Toepler pumps with a contact volume of 70 cc. were used. For the separation of argon from krypton the charcoal temperature was that of solid carbon dioxide – acetone or about −78° C., and for the separation of krypton from xenon a charcoal temperature of −20° C. was used. Glückauf points out that in optimal conditions, and where the amounts of gases to be separated are similar, the number of operational cycles producing the most effective separation of any two gases should be about twice the number of adsorption units. In our apparatus, the conditions were not quite optimal, and it was found experimentally that a separation at −78° C. of 24 operations removed 95% of the argon from a ternary mixture without any krypton getting through. The remaining 5% of the argon, together with the krypton and xenon, was then returned to the first unit of the separator and separated again, using 27 operations. This removed altogether 99.95% of the argon, together with a known 1% of the krypton. The remaining krypton and xenon were now returned to the first unit of the separator and the charcoal temperature raised to −20° C. Twenty-four operations at this temperature separated 95% of the remaining krypton, and, with the 5% of krypton and 100% of the xenon returned to the first unit, a further 24 operations separated all but 0.25% of the krypton which was left in the xenon.

Before the separator was used on fission gases, it was tested thoroughly with known mixtures of argon, krypton, and xenon. Purity of the products was checked by their adsorption behavior over charcoal at different temperatures and mass spectrometrically by Thode and Graham.

Results

Samples of rare gases were extracted from disks from two slugs. The two slugs were irradiated separately and under slightly different conditions. The results are given in Table I.

TABLE I

VOLUMES OF ARGON, KRYPTON, AND XENON IN SAMPLES OF URANIUM

Sample	Wt., gm.	Vol. of gas $\times 10^{-3}$ cc. at N.T.P.	Vol. $\times 10^{-5}$ cc. at N.T.P./gm. U
Specimen *A*	48.2	A: 2.80 Kr: 0.31 Xe: 1.56	A: 5.81 Kr: 0.64 Xe: 3.24
Specimen *B*	135.4	A: 3.03 Kr: 1.03 Xe: 5.22	A: 2.24 Kr: 0.76 Xe: 3.85

The ratios of total xenon to total krypton for specimens A and B are 5.03 and 5.07 respectively.

In Tables III and IV of their paper, Thode and Graham (3) summarize the abundance data for isotopes of xenon and krypton respectively. If the figure of 5.05 is taken as the ratio of xenon to krypton, we can tabulate the relative fission yields of masses 83, 84, 85, 86, 131, 132, 134, and 136, that of xenon 134 being taken as standard (Table II).

TABLE II

RELATIVE FISSION YIELDS

Mass No.	Relative fission yield	Mass No.	Relative fission yield
83	0.0779	131	0.381
84	0.148	132	0.566
85	0.0390	134	1.000
86	0.286	136	0.829

For the investigation of krypton for radioactivity a Geiger–Müller counter was constructed such that a small specimen of krypton could be mixed with the filling of argon and alcohol. A volume of 1.7×10^{-4} cc. at N.T.P. of fission krypton was put into a pipette that delivered a fraction 1/1056 to the counter. When this was mixed with the filling, a count of 27,600 per minute was obtained. This showed that at any rate one of the krypton isotopes must be radioactive, and because of the age of the uranium specimen, long lived. This is now believed to be krypton 85*, an isomer of the 4.0 hr. krypton 85.

Taking the percentage of krypton 85 to total krypton in the sample as 7.43%, and further assuming that every disintegration occurring within the cathode of the counter was counted, a specific activity for krypton 85 could be calculated giving the half life of the isotope. Using this technique the half life was estimated to be of the order of 16 years; Thode and Graham (3) obtained a more accurate estimate of 9.4 ± 0.4 years from a study of the decrease of the relative abundance of mass 85 in a specimen of fission krypton over a decay period of 440 days. The discrepancy in the estimated half lives is almost certainly due to counting inefficiency associated with the high counting rate used. A repetition of the experiment with a smaller amount of krypton would have provided presumably a value closer to that of Thode and Graham.

A similar experiment with fission xenon failed to give any conclusive evidence of the existence of a long-lived active xenon isotope.

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appreciation of the co-operation of Professor Thode and Mr. Graham by whose mass spectrometric technique so much information was obtained from such small gas samples.

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A PRELIMINARY STUDY OF THE PERMEABILITY OF CELLOPHANE TO LIQUIDS[1]

By S. Madras,[2] R. L. McIntosh,[3] and S. G. Mason

Abstract

The permeability of swollen cellophane accommodated by solvent exchange to a variety of liquid permeants has been studied. The degree of swelling, as measured by the thickness, has been shown to be retained when the swelling agent is removed by solvent exchange. Progressive swelling causes a controllable increase in the permeability to a given liquid, but the permeability coefficient at a given thickness is specific for the liquid. For water and aqueous solutions, K is about five times that of organic permeants. Values for the organic liquids are all of the same order of magnitude and show systematic variation with the degree of swelling. For homologous series of alcohols and ketones, K decreases with increasing chain length. Attempts to calculate the effective pore radius and pore number from K and the void fraction were successful only for water and dilute sodium hydroxide solutions, where a radius of 1.5×10^{-7} cm. and a pore number of 10^{13} per cm.^{2} were obtained. An independent method based on combined permeability and electrical conductance yielded a value of 3×10^{-7} cm. for the effective pore radius. With organic permeants, it is believed that complications introduced by swelling invalidate the application of the equations. The results obtained can be explained on the basis of viscous flow of the liquids through a porous network in which the number and dimensions of the pores vary with the degree of swelling, but evidence in favor of the validity of this mechanism is inconclusive.

Introduction

Cellophane possesses a number of properties that render it useful as a semipermeable membrane and it has as a result found increasing application in ultrafiltration (13), dialysis (11), and osmometry (3, 14). Several brief investigations of the microstructure of cellophane materials have been carried out and have served to throw light on the mechanism of liquid permeability. It has been concluded from these studies that a Poiseuille type of viscous flow through a porous network occurs (17). McBain and Kistler (8) showed that the liquid permeability could be increased by swelling in water, and that a substantial portion of this increase could be retained after the water was removed by solvent exchange. Morton (13) showed that a further increase was obtained by swelling in solutions of sodium hydroxide.

This communication deals with a preliminary study of the permeability of cellophane to various liquids, including a number commonly used as solvents in osmotic pressure measurements, and the relation of permeability to the degree of swelling. Attempts were made to estimate the effective size of capillaries under various conditions of swelling from the permeability coefficient, the void fraction, and the measured thickness of swollen cellophane membranes, following a method originally used by Bechhold (1) and subsequently developed by other workers for collodion membranes (5). A partially

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independent method based on permeability and electrical conductivity measurements using aqueous permeants was employed as a check on the validity of this method and was found to give substantially different results. These are subsequently referred to as the permeability – void volume and permeability–conductance methods and are described briefly below.

Permeability – Void Volume Method

The volume of viscous flow Q in unit time through unit cross section of a porous material of thickness L under a pressure gradient Δp may be expressed as

$$Q = P\Delta p = \frac{K\Delta p}{\eta L}, \tag{1}$$

where η is the viscosity of the permeant, and P and K respectively the permeability and the permeability coefficient of the porous medium.

If the capillary structure and the laws governing flow through a single capillary are known, K can in principle be predicted.

A generalized expression for K is given by the Kozeny–Carman equation (16) which for our purposes is most conveniently expressed in the form:—

$$m = \sqrt{\frac{k_0 K}{\epsilon\ \overline{\cos^2\theta}}} = \sqrt{\frac{k\ .K}{\epsilon}}. \tag{2}$$

In this equation m is the mean hydraulic radius $\left(\frac{\text{wetted area}}{\text{wetted perimeter}}\right)$ of the pores in the capillary structure, k_0 is a shape factor determined by the geometry of the pores, and ϵ is the fractional void volume available for liquid flow. $\overline{\cos^2\theta}$ is averaged over all pore orientations between the direction of the pore and the direction of macroscopic flow of the liquid.

It is evident from Equation (2) that prior knowledge of the capillary structure is necessary before the appropriate value of k can be selected. For this reason, permeability measurements alone will not reveal details of structure but can merely serve for the calculation of equivalent pore dimensions in terms of an assumed model. In practice k varies from 2 to 6 between the extreme cases of (*a*) a network of identical cylindrical capillaries parallel to the direction of macroscopic flow and (*b*) the interstices between cylinders at right angles to the direction of macroscopic flow (16). Despite the marked parallel alignment of the molecular chains in a sheet of cellophane, which would tend to favor model (*b*), we consider the simple model (*a*).

For unrestricted Poiseuille flow through a network of N independent cylindrical capillaries per unit area arranged parallel to the direction of macroscopic flow and of equal radius r,

and

$$\left.\begin{aligned} K &= \frac{\pi r^4 N}{8} \\ \epsilon &= \pi r^2 N \end{aligned}\right\}. \tag{3}$$

Combining these equations, we obtain

$$r = 2m = \sqrt{\frac{8K}{\epsilon}} \tag{4}$$

and

$$N = \frac{\epsilon^2}{8\pi K}. \tag{5}$$

Equation (4) has been used extensively to compute the pore size of collodion membranes (5). Manegold and Viets (11) and Morton (13) applied it to regenerated cellulose membranes of the cellophane type.

In spite of the assumptions implied in deriving these equations, notably the oversimplified model of the capillary network rather than the more probable interconnecting web of tortuous pores of various size, the existence of Poiseuille flow unrestricted by electrokinetic and steric effects, and the assumption that the permeant is imbibed only in pores that are completely available for liquid flow, Elford and Ferry (4) concluded that the error in the average pore radius of collodion type membranes determined in this way should not exceed 25% provided r exceeds 10^{-6} cm.

Permeability-conductance Method

The determination of the permeability coefficient and the calculation of pore size by the above method depend on the knowledge of the void fraction and thickness of the membrane. Because of the peculiar swelling properties of cellophane a certain amount of doubt existed as to the validity of the measured values of these quantities. An alternative method that involves neither the thickness nor the void fraction of the membrane makes use of the electrical conductance corrected for surface conductance when the membrane is saturated with potassium chloride solutions of known concentration. Assuming a parallel-cylindrical network and that Ohm's law applies, we may write

$$C = \frac{\pi r^2 N \kappa}{L} \tag{6}$$

where κ is the specific conductivity of the permeant and C is the over-all conductance per unit area. Combining this relation with Equation (3) we obtain

$$r = \sqrt{\frac{8\eta\kappa P}{C}}. \tag{7}$$

A related method based simply on the measured conductance and void fraction has been used with some success on collodion membrane (7, 10).

Experimental Part

Materials

Canadian Industries Limited Cellophane grade No. 600 P.T. (not waterproofed) was used throughout this investigation. The thickness of the dry sheet was 0.004 cm.

All organic liquid permeants used were C.P. grade with the exception of ethanol and were further purified by a distillation. Absolute ethanol was prepared by the standard method using calcium oxide.

Potassium chloride solutions for the conductivity experiments were prepared from Reagent Grade potassium chloride and conductivity water of specific conductance less than 10^{-6} mho per cm.

Preparation of Membranes

The glycol plasticizer was removed from the cellophane by immersion in water at 60° C. for two hours. When degrees of swelling below that obtained in water were desired, 60% ethanol was substituted at this stage, and the thickness was adjusted by a further immersion for a period of at least 12 hr. in ethanol solutions of various concentrations. Typical results of the latter treatment are shown in Table I.

TABLE I

ADJUSTMENT OF MEMBRANE THICKNESS

Swelling solution		L, cm. $\times 10^3$
% Water	% Ethanol	
40	60	4.2 – 4.5
50	50	4.9 – 5.0
60	40	5.9 – 6.2
80	20	7.7 – 7.9
100	0	8.3 – 8.5

After this treatment, the membranes were washed with ethanol–water solutions of increasing ethanol content, in order to remove the water, and were then stored for at least four hours in absolute ethanol. This treatment did not decrease their thickness. They were then kept in anhydrous acetone until used. Prolonged storage in acetone was found to have no effect on the permeability or thickness of the membrane. With the exception of the washing stage this preparation was similar to that used by Carter and Record (3). Storage in ethanol and other alcohols was found to result in a gradual decrease in permeability.

Membranes intended for conductivity measurements were rinsed repeatedly in distilled water, after the plasticizer was removed by water immersion as described above. These membranes were stored in conductivity water, being transferred to their respective potassium chloride solutions at least 24 hr. before being used.

Highly swollen membranes were prepared by immersion of water-washed material in sodium hydroxide solutions. The sodium hydroxide was removed by repeated rinsing in distilled water until it could no longer be detected in

an ash test. The membranes were then stored in conductivity water, or in acetone after accommodation through successive alcohol washings as described above.

Permeability and Conductance Measurements

Most of the permeability measurements were carried out in brass cells similar in design to that of the Van Campen osmometer (2) modified to allow operation in permeability measurements in the same manner as with the combined permeability–conductance cell. The latter cell consisted (Fig. 1)

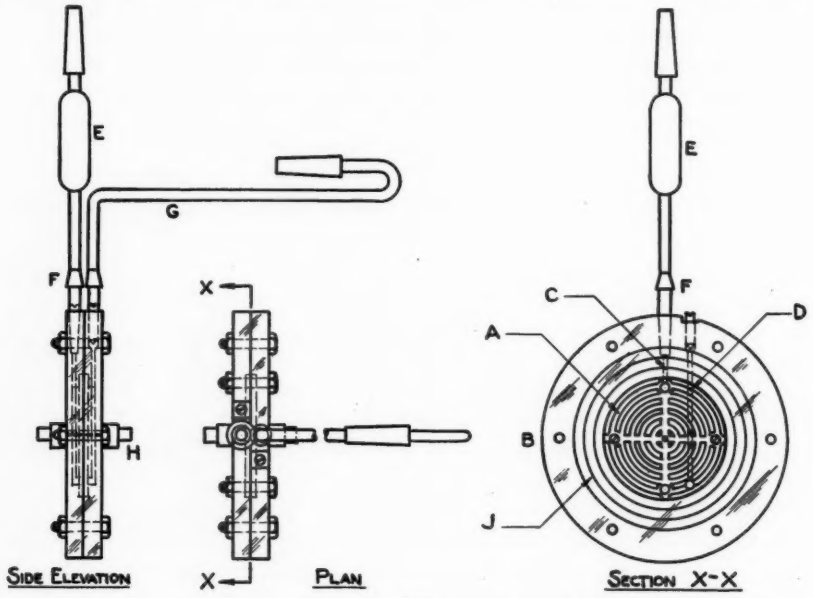

FIG. 1. *The permeability–conductance cell.*

of two machined Lucite half-cells between which the membrane was clamped by means of six symmetrically placed bolts. To obtain a leak-proof seal three concentric rings were cut into one of the half-cell faces to fit corresponding ridges on the face of the other half-cell. A brass disk *A* with machined annular and radial slots was screwed into a circular recess in the center of each wall with its grooved surface countersunk 2×10^{-3} cm. below the cell face. The two disks were platinum plated and served both as membrane supports and electrodes. A binding post *H* connected to each electrode served as an external contact. The glass reservoir *E* for permeant supply and an open calibrated horizontal capillary *G* for observing the rate of flow were attached to the holes *C* by means of standard taper joints. The channel *D* in each half-cell was sealed with a screwed tapered plug and was used for filling and venting.

The cells were placed in an air thermostat maintained at $30.0 \pm 0.1°$ C.

In carrying out a permeability measurement, the membrane was first accommodated to the permeant by transferring it from the acetone and immersing it in the permeant for at least two hours. The thickness of the immersed membrane was measured with a micrometer caliper. Several readings were taken with a mean deviation of about 5%. The rate of flow of the permeant through the membrane under a given pressure gradient was observed in the capillary G (Fig. 1) over a period of about two hours. The pressure was applied by means of air in the reservoir E and was measured on a differential xylene manometer. A series of such flow rates at different pressure gradients, both positive and negative, was determined.

A plot of flow rate versus pressure gradient always yielded a straight line. The slope of this line provided an average value of the flow rate under unit pressure gradient without any need of a correction for capillarity in the flow tube G. A deviation from linearity indicated a leak in the system and such results were discarded.

In calculating the permeability coefficient K, it was assumed that the area of membrane accessible to flow was the "free area", i.e., the total area of membrane in the cell less that of the ridges of the supporting plates D, which were impressed on the membrane surface. It was established experimentally that this assumption led to absolute permeability coefficients which were as much as 10% too low.

Conductances were measured on a Jones Conductance Bridge, using an external shunt on one ratio arm to provide a ratio of 1 to 11. This was found necessary to give adequate sensitivity at the low values of resistance found.

A standard conductance cell was used as an auxiliary in order to measure the conductance of the solution before and after contact with cellophane. These duplicate measurements were made to ensure that no further adsorption on the membrane had occurred during a permeability measurement. No change in conductivity was noted when using membranes that had been stored more than 12 hr. in the permeant. On completion of each permeability-conductance experiment the cell was opened, the membrane removed, and the cell reassembled without any membrane. It was then refilled with the same solution and the resistance again measured. The resistance of the membrane was taken to be the difference of the two measured resistances.

Determination of Imbibition

Several methods were tried, all based on the principle of weighing the liquid imbibed in the membrane. The method finally adopted consisted in measuring the rate of drying of the membrane. It was found that the drying curve consisted of two straight lines of different slope corresponding to two different rates of drying. The point of intersection was assumed to correspond to the point of transition between evaporation of liquid from the surface and from the interior of the membrane.

A piece of cellophane, accommodated to the permeant, cut square so that its area could be determined readily, was blotted free of the bulk of the liquid adhering to the surface and suspended vertically on the weighing arm of a chainomatic balance. Its weight was taken every 30 sec. for about 20 min. A typical curve is shown in Fig. 2. After this weighing, the cellophane was

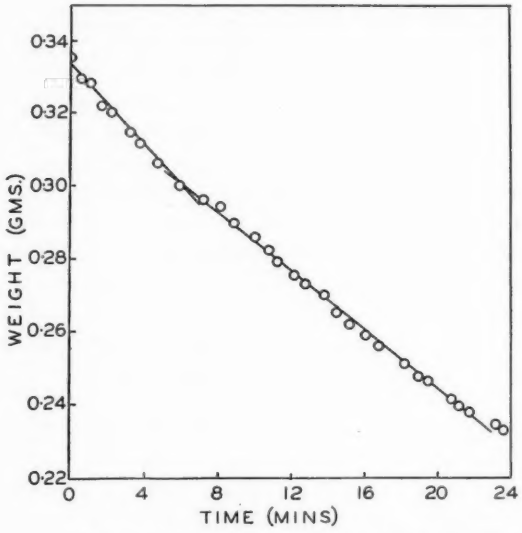

FIG. 2. *Drying curve of a water soaked membrane.*

dried in an oven at 130° C. for a period of two hours, and its dry weight determined. The difference between the interpolated value of the wet cellophane and the dry weight was taken to be the weight of the imbibed liquid. The pore volume per unit area was obtained by dividing this weight by the area of the cellophane and the density of the liquid. With aqueous solutions, the weight of residual solute was negligible.

The drying rate method was found to give more reliable and consistent results than the conventional method of blotting the soaked membrane free of excess liquid and weighing (5).

Results

Effect of Viscosity

In order to check the validity of Equation (1), the permeability P of water through the swollen membrane was measured at various temperatures. The results, given in Table II, indicate that at a fixed degree of swelling P varies inversely with the viscosity of the permeant. This together with the fact that in all cases the rate of flow Q was found proportional to the pressure gradient is taken as fairly conclusive evidence of a viscous type of flow.

TABLE II

EFFECT OF VISCOSITY ON THE PERMEABILITY OF A WATER SWOLLEN MEMBRANE

T,° C.	P, gm.$^{-1}$ cm.^{2} sec. $\times 10^{11}$	η (poises) $\times P \times 10^{13}$
20	1.95	1.95
25	2.17	1.93
28	2.28	1.91
33.5	2.65	1.97
38	3.08	2.02
40	3.30	2.07

Effect of Swelling on Permeability

A large number of determinations of the permeability of various liquids was made at various degrees of swelling. Table III includes the data obtained

TABLE III

EFFECT OF SWELLING ON PERMEABILITY COEFFICIENT

Permeant	Membrane treatment	L, cm. $\times 10^3$	K, cm.^{2} $\times 10^{16}$
Water	Water	8.0	15.8
3%NaOH	3% NaOH	9.5	21.3
6% NaOH	6% NaOH	10.5	25.6
Methanol	60% Ethanol	4.5	0.94
	Water	7.7	3.57
	3% NaOH	9.5	5.22
Ethanol	60% Ethanol	4.5	7.52
	Water	7.7	2.58
	3% NaOH	10.0	4.17
Acetone	60% Ethanol	4.5	0.87
	Water	8.0	3.07
	3% NaOH	9.0	5.00

using methanol, ethanol, acetone, water, and sodium hydroxide solutions as permeants. It will be noted from this table and a plot of K versus membrane thickness (Fig. 3) that an approximately fourfold increase in the permeability coefficient of the organic permeants resulted from increasing the thickness from 4.5×10^{-3} cm. by swelling in water. Additional swelling by treatment of the membrane with sodium hydroxide caused a further increase in permeability. Similar results obtained with a variety of alcohols, ketones, and miscellaneous organic liquids are shown in Table IV.

The most striking feature of these results is that the permeability coefficients corresponding to a given membrane thickness fall into two clearly distinct classes, one for organic and the other for aqueous permeants. Thus

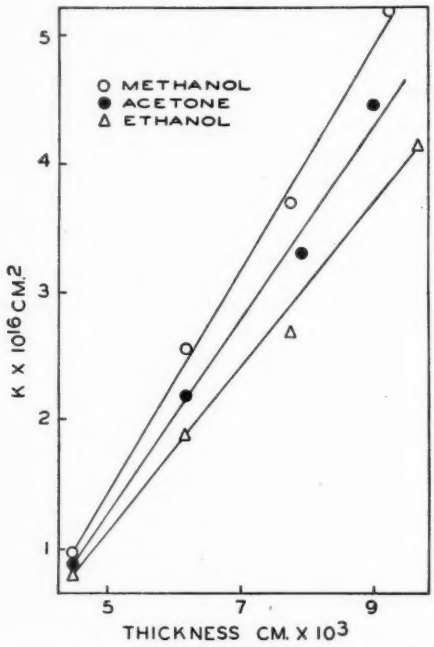

FIG. 3. *Variation of permeability coefficient with thickness of swollen membranes.*

for water swollen membranes having approximately the same thickness, K of organic liquids was about one-fifth that of water.

Permeability to Homologous Series

Permeability determinations were made with homologous series of liquids on treated membranes to observe the effect of lengthening of the carbon chain. The series included alcohols and ketones. A number of miscellaneous liquids were also examined, including chloroform and carbon tetrachloride because of their frequent use in osmometry.

Values of the thickness, permeability, and permeability coefficients are given in Table IV. In addition to the effect of swelling in increasing P and K, attention is drawn to the following points.

(1) Corresponding to a given membrane treatment, the resulting membrane thickness is approximately the same for all permeants except in the case of the ketones, where a decrease in thickness with increasing chain length is shown.

TABLE IV

PERMEABILITY OF ORGANIC LIQUIDS

Permeant	60% Ethanol			Water			3% NaOH		
	L, cm. $\times 10^2$	P, gm.$^{-1}$cm.^{3} sec. $\times 10^{11}$	K, cm.$^3 \times 10^{16}$	L, cm. $\times 10^2$	P, gm.$^{-1}$cm.^{3} sec. $\times 10^{11}$	K, cm.$^3 \times 10^{16}$	L, cm. $\times 10^2$	P, gm.$^{-1}$cm.^{2} sec. $\times 10^{11}$	K, cm.$^3 \times 10^{16}$
Alcohols									
Methanol	4.5	0.41	0.94	7.7	0.92	3.6	9.5	1.1	5.2
Ethanol	4.5	0.17	0.75	7.7	0.35	2.6	10.0	0.33	4.2
Propanol	4.5	0.083	0.64	7.7	0.16	2.1	9.5	0.21	3.4
Butanol	4.5	0.061	0.61	7.7	0.11	1.8	9.0	0.12	2.6
Ketones									
Acetone	4.5	0.60	0.87	8.0	1.30	3.1	9.0	1.9	5.0
Butanone-2	4.5	0.44	0.72	8.0	0.96	2.8	8.8	1.4	4.7
Pentanone-2	4.5	0.29	0.63	7.5	0.78	2.7	8.5	1.1	4.4
Hexanone-2	4.5	0.24	0.58	7.0	0.68	2.5	8.0	1.0	4.2
Heptanone-4	4.5	0.16	0.51	6.2	0.55	2.4	7.5	0.74	3.9
Octanone-2	4.5	0.13	0.45	6.0	0.45	2.0	7.5	1.0	3.6
Miscellaneous									
Ethyl acetate	4.5	0.38	0.69	7.5	0.50	1.4	8.5	0.53	1.8
Methyl propionate	—	—	—	7.6	0.48	2.2	8.0	0.54	1.8
Ethyl propionate	—	—	—	7.6	0.42	1.3	8.0	0.47	1.7
Chloroform	4.5	0.27	0.62	7.5	0.34	1.3	8.0	0.31	1.4
Carbon tetrachloride	4.5	0.13	0.52	7.5	0.17	1.1	8.0	0.19	1.2
Benzene	—	—	—	7.5	0.26	1.1	8.0	0.26	1.2
Toluene	—	—	—	7.6	0.24	1.0	8.0	0.24	1.0
Nitrobenzene	—	—	—	7.6	0.09	1.2	—	—	—
Hexane	—	—	—	7.6	0.36	0.85	8.0	0.40	1.0
Heptane	—	—	—	7.6	0.26	0.76	8.0	0.30	0.88

(2) For a given membrane treatment, the permeability coefficients of the homologous series of alcohols and ketones decrease progressively with increasing number of carbon atoms. The effect is shown for the ketones in Fig. 4.

(3) The permeability coefficients of the liquids that are insoluble in water, mainly in the miscellaneous group, are consistently lower than those of the water soluble liquids. The data on this group also show that water and caustic treatments cause relatively small increases in K.

(4) There is little difference in K for benzene and nitrobenzene. Since Martin and Gortner (12) report that in the presence of benzene and nitrobenzene, the respective zeta potentials of cellulose are zero and -142 mv., this indicates the absence of appreciable electroviscous effects.

Void Volume and Capillary Structure

In order to compute the effective pore radius and pore number by means of Equations (4) and (5) it was necessary to know the void fraction ϵ. This was computed by dividing the volume of liquid imbibed per unit area (as

determined by the weighing method) by the measured membrane thickness. This procedure assumes that all the imbibed liquid is contained in pores and is available for liquid flow.

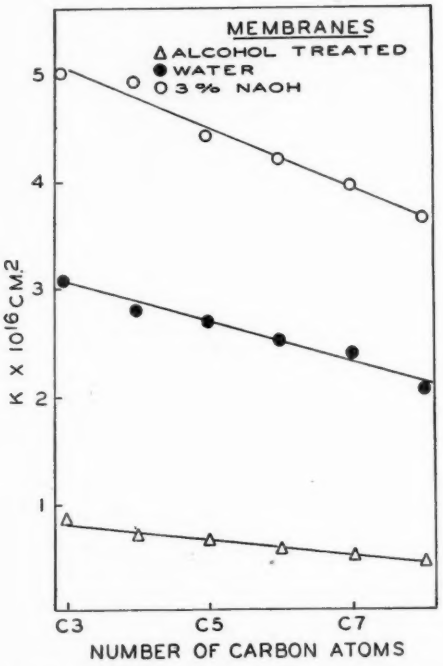

FIG. 4. *Variation of the permeability coefficient of ketones with number of carbon atoms for different membrane treatments.*

Since the volumes of a mixture of cellulose and a liquid that does not react chemically with the cellulose are additive (6), ϵ can be calculated from the relation

$$\epsilon = 1 - \frac{0.62\,W}{L},$$

where 0.62 is the specific volume of cellulose and W is the weight of cellulose in grams per square centimeter of swollen membrane. This should apply to all the permeants listed in Tables III and IV with the possible exception of the sodium hydroxide solutions.

Values of ϵ obtained by the two methods are given in Table V. Good agreement is shown only with water and 3% sodium hydroxide. The two methods give self-consistent results with 6% sodium hydroxide, but there is a significant difference between the two sets. In the case of the alcohols, there is wide divergence. Values of ϵ calculated from the void

TABLE V

COMPARISON OF VALUES OF VOID FRACTION

Permeant	Membrane treatment	ϵ	
		From void volume	From thickness
Water	Water	0.64	0.62
		0.62	0.615
3% NaOH	3% NaOH	0.54	0.54
6% NaOH	6% NaOH	0.55	0.66
	6% NaOH	0.56	0.66
	6% NaOH	0.54	0.67
Methanol	60% Ethanol	0.18	0.38
	Water	0.17	0.59
	3% NaOH	0.17	0.62
Ethanol	60% Ethanol	0.21	0.38
	Water	0.12	0.59
	3% NaOH	0.10	0.62
Propanol	60% Ethanol	0.32	0.38
	Water	0.18	0.56
	3% NaOH	0.16	0.63
Butanol	60% Ethanol	0.27	0.37
	Water	0.20	0.59
	3% NaOH	0.14	0.62

volume are much lower than those computed from the thickness. Similar differences were shown for the remaining permeants listed in Table IV.

The discrepancy between the values obtained by the two methods for the organic permeants reveals an error in one or both methods. The simplest explanation, which is discussed later, is that effective thickness is incorrectly measured as the result of a structural contraction which is not detected by the micrometer caliper. If such is the case both values are in error since the thickness measurement is used in computing both quantities. This will have the further effect of yielding values of K, which, for purposes of calculating capillary dimensions, are spurious, since the permeability coefficient is computed from the measured P and the membrane thickness.

If Equations (4) and (5) are applicable, we are justified only in using the K and ϵ values for water and 1% sodium hydroxide and 3% sodium hydroxide to compute the effective pore radius and the pore number. These values are shown in Table VI and include the data for 6% sodium hydroxide, ϵ being taken to be 0.55. The value of r computed for the water in water swollen membrane thus obtained compares favorably with values of 2 to 3 $\times$ 10^{-7} cm. calculated by McBain and Kistler (8) from the pressure required to blow air through a water soaked cellophane and 1.3 $\times$ 10^{-7} cm. estimated by

TABLE VI

AVERAGE PORE RADIUS AND PORE NUMBER

Permeant	Treatment of membrane	Average pore radius, cm. $\times 10^7$	Pore number $\times 10^{-12}$/cm.^{2}
Water	Water	1.4	9.1
3% NaOH	3% NaOH	1.7	5.6
6% NaOH	6% NaOH	2.0	2.2

Manegold and Viets (11) using the permeability – void volume method. It is interesting to note that these values of the pore radii are similar to those of collodion membranes of void fraction *circa* 0.60 (5).

Permeability-conductance Measurements

The results of a series of permeability conductance measurements on water swollen membranes, using potassium chloride solutions ranging from 0.002 *M* to 0.1 *M*, are given in Table VII. It will be noted that the *P* values are

TABLE VII

PERMEABILITY-CONDUCTANCE DATA FOR WATER SWOLLEN CELLOPHANE

Molarity KCl	P, gm.$^{-1}$ cm.^{2} sec. $\times 10^{11}$	C, mhos cm.$^{-2}$ $\times 10^2$	κ/C, cm. $\times 10^2$
0.002	2.38	1.12	2.60
0.005	2.26	2.01	3.53
0.008	2.46	2.61	4.35
0.010	2.21	3.08	4.60
0.020	2.15	5.05	5.39
0.040	2.46	8.53	6.37
0.060	2.58	11.92	6.64
0.080	2.52	15.25	6.79
0.100	2.14	18.73	6.92

reasonably constant. Values of κ/C on the other hand increase progressively with increasing concentration as the result of surface conductance, which tends to give high values for *C*. These results are similar to those obtained by Manegold and Solf (10) for potassium chloride solutions in collodion membranes of pore radii ranging from 6.5×10^{-7} to 20×10^{-7} cm., except that κ/C reached a constant value above 0.03 *M*.

To eliminate the error due to surface conductance, values of κ/C are plotted against (concentration)$^{-1}$ and extrapolated to infinite concentration, at which point surface conductance is believed to become negligible (Fig. 5). This yields a κ/C value of 7.5×10^{-2} cm. The value of r calculated from these data using Equation (7) is 3.4×10^{-7} cm. This is 2.5 times as great as that computed from the permeability – void fraction data of water in water swollen

cellophane. This agreement however is illusory, as can be seen by computing the effective void fraction from the conductivity and thickness. A comparison of Equations (3) and (6) shows that $\epsilon = \frac{LC}{\kappa}$, from which ϵ is calculated to be 0.11, i.e., about 1/6 the value given in Table V for water. Manegold and

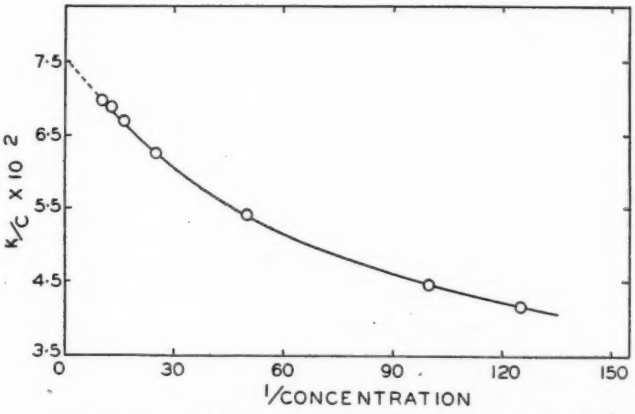

FIG. 5. *Extrapolation of κ/C to eliminate surface conductance effect.*

Solf (10), in the measurements on collodion membranes referred to above, found that this ratio had a value of from 1/3 at low pore sizes increasing with increasing pore sizes to 2/3, and they attributed the effect to an irregular slit structure, together with possible closed pores.

If instead of the simple cylindrical capillary network, a more general structure is assumed with pores of any shape and various orientations θ to the normal of the sheet and that Ohm's law applies, it is readily shown that Equation (6) assumes the form:—

$$\frac{LC}{\kappa} = \overline{\cos^2 \theta} \cdot \epsilon \ .$$

Thus if the entire imbibed volume is operative in electrical conduction, as it is assumed to be in liquid permeation, $\overline{\cos^2 \theta} = 1/6$ for the water swollen cellophane. For orientation normal to the sheet $\overline{\cos^2 \theta} = 1$ and for random orientation $\overline{\cos^2 \theta} = 1/2$. Hence if the conductivity method is valid the results indicate the existence of either closed pores or marked pore orientation in the plane of the sheet. The results, while not conclusive, therefore cast doubt on the validity of using the measured void volume in Equation (2).

Discussion

It is evident from these results that the rate of flow of liquids through cellophane is not defined by a permeability coefficient which depends solely on the thickness of the swollen sheet.

It has been demonstrated for the case of water that viscous type flow occurs, i.e., the rate of flow varies directly with the pressure gradient and inversely with the viscosity. The method of liquid replacement followed in accommodating swollen membranes to the various permeants produces little change in the thickness of the membrane and hence presumably in the degree of swelling. This agrees with current views on the phenomena of swelling in cellulose (15).

An increase in thickness results in an increased K, although the increase depends upon the nature of the permeant. This is of considerable practical importance in preparing cellophane membranes in osmometry, as has been pointed out by McIntosh *et al.* (14). The relatively small increase in the case of water-insoluble permeants is of interest and may be partly attributed to incomplete removal of the water. The small variation in K of various organic liquids can be attributed jointly to small variations in the degree of swelling as measured by the thickness and to steric effects.

The large differences in permeability between aqueous and organic permeants through membranes of the same thickness is however entirely inconsistent with the Bechhold (1) type of capillary structure, unless the additional assumption is made that internal changes in the capillary network occur that do not reveal themselves by changes in external dimensions.

The measured values of the void fraction show a similar anomaly. Only in the case of water and 1% sodium hydroxide solutions do the values calculated from the imbibition-thickness and the thickness alone agree. With the organic permeants there is a large discrepancy between the two sets of values. Moreover, the volumes of organic liquids imbibed are less than half those of aqueous solutions at the same membrane thickness.

The only explanation that we can offer at the present time is that, on replacing the water by any of the organic permeants listed in Table IV, a reduction in the degree of swelling occurs that is not detected in measuring the thickness. This may be envisaged as a microscopic or submicroscopic wrinkling of the surface that does not materially change the distance separating the "high spots" in the structure. Since cellophane is precipitated in an aqueous medium, i.e., the sheet is formed in the water swollen state, this hypothesis explains why agreement in the void fraction values is obtained with water. It also explains the anomalies between the permeabilities and void fractions of water and organic liquids.

The difference in the results of the permeability – void volume and permeability–conductance methods is difficult to account for except by imposing further qualifications of the capillary network structure.

Thus, while the results presented here can be explained by a mechanism of viscous flow through a capillary network whose internal dimensions are determined jointly by the thickness and the permeant, the evidence in favor

of such a mechanism is inconclusive. It is our belief however that permeability measurements provide a useful method of studying the phenomenon of swelling of cellulose, and are being studied further.

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